

A field investigation of the relationship between zinc and acid volatile sulfide concentrations in freshwater sediments

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Abstract

Understanding relationships between cationic metals such as cadmium, copper, nickel, lead and zinc, and amorphous iron sulfides, measured as acid volatile sulfide (AVS), is key to predicting metal bioavailability and toxicity in sediments. The objective of the present study was to assess seasonal and spatial variations of AVS in freshwater sediments contaminated with zinc. Sediments were sampled from three streams with varying levels of zinc contamination at two different times, March and June of 1995, representing cold- and warm-weather situations. Interstitial (pore) water concentrations of zinc, and solid phase concentrations of AVS and zinc were measured in surficial and deep sediment horizons. Toxicity tests (10-d) with the amphipod *Hyaella azteca* were conducted using intact cores. Sediment zinc concentrations from six sites within the primary test stream differed by about five-fold, and also varied seasonally. Acid volatile sulfide concentrations were generally lower than those of zinc, and pore water zinc concentrations typically were elevated. There was a positive correlation between solid-phase AVS and zinc concentrations, suggesting that the system was dominated by zinc, as opposed to iron sulfides. In contrast to expectations arising from some studies of seasonal variations of AVS in iron-dominated systems, AVS concentrations were smaller in June than in March. However, this was likely due to a major storm event and associated sediment scouring before the June sampling, rather than to seasonal processes related to variations in temperature and dissolved oxygen. Based upon an indirect analysis of depth variations in AVS, there was some indication that zinc sulfide might be less prone to oxidation than iron sulfide. There was a strong correlation between toxicity of the sediment samples to *H. azteca* and interstitial water concentrations of zinc; however, the possible contribution of other contaminants to sediment toxicity cannot be dismissed.

1. Introduction

Sediments serve as the ultimate repository of recalcitrant contaminants, such as organochlorines, polycyclic aromatic hydrocarbons (PAHs) and metals that enter aquatic ecosystems. Hence, there has been significant interest in the development of methods and models for predicting the effects of sediment-associated contaminants on benthic communities. One of the challenges in making these types of effects pre-

dictions is identification of that fraction of the total sediment contaminant load which is biologically available. Early studies by Adams et al., (1985) and Swartz et al., (1985) demonstrated that, while dry weight pesticide or metal concentrations in sediments were not useful for predicting toxicity to benthic organisms, interstitial (pore) water concentrations were correlated with the amount of bioavailable contaminant. Thus, those sediment characteristics that control concentrations of contaminants in pore water are key to evaluat-

ing bioavailability and effects. For nonionic organics, such as some pesticides and PAHs, organic carbon is the predominant sedimentary phase controlling pore water contaminant partitioning; this fact has been utilized in the development of sediment quality criteria (SQC) for these types of chemicals (Di Toro et al., 1991). In the case of metals, pore water concentrations in many sediments appear to be controlled through the formation of metal-sulfide complexes arising from the interaction of cationic metals with the amorphous sulfide fraction commonly termed acid volatile sulfide or AVS (Cornwell & Morse, 1987; Di Toro et al., 1990; Slotten & Reuter, 1995). In uncontaminated sediments, AVS is comprised primarily of iron monosulfides; however, a number of divalent metals of environmental concern, including cadmium, copper, lead, nickel and zinc, effectively displace the iron, thereby forming insoluble, biologically-unavailable sulfide complexes (Di Toro et al., 1992). Laboratory experiments with metal-spiked and field-collected marine and freshwater sediments have demonstrated that when AVS concentrations (on a molar basis) exceed those of metals simultaneously extracted with the AVS (simultaneously extracted metals; SEM) pore water metal concentrations are minimal, and acute or chronic toxicity to a variety of benthic species does not occur (Di Toro et al., 1990; Ankley et al., 1991; Carlson et al., 1991; Casas & Crecelius, 1994; Pesch et al., 1995; Berry et al., 1996; DeWitt et al., 1996; Hansen et al., 1996a; Sibley et al., 1996). Moreover, a series of field colonization experiments with spiked sediments have corroborated the results of laboratory tests, i.e., when there is sufficient AVS to bind the SEM, normal benthic communities are present (Hare et al., 1994; Hansen et al., 1996b; Liber et al., 1996).

Based on these studies, the U.S. Environmental Protection Agency (EPA) has proposed that one of several approaches to deriving SQC for metals would be direct comparison of molar AVS and SEM concentrations (Ankley et al., 1994, 1996). One of the potential drawbacks with this proposal has been the observation that AVS concentrations in uncontaminated sediments (hence, iron sulfide) can vary markedly over different seasons (e.g., Howard & Evans, 1993; Leonard et al., 1993). Under aerobic conditions, this temporal variability is manifested in lower concentrations of AVS during cold-weather months, presumably due to a constant rate of oxidation of the iron sulfide coupled with a decrease in the generation of sulfide by sulfate-reducing bacteria at cooler temperatures (Herlihy & Mills, 1985). Another issue associated with the

use of SEM:AVS relationships to derive SQC is the fact that surficial concentrations of AVS (e.g., 0–3 cm) tend to be smaller than those in deeper horizons of clean sediments, again presumably due to oxidation of iron sulfide complexes (Howard & Evans, 1993; Brumbaugh et al., 1994; Hare et al., 1994; Besser et al., 1996; Hansen et al., 1996b; Leonard et al., 1996; Liber et al., 1996). This evidence of temporal and spatial variation of AVS has led some to be critical of attempts to predict metal bioavailability using this paradigm (Luoma & Carter, 1993; Meyer et al., 1994).

Recent studies, however, have indicated that estimates of temporal and spatial variations in AVS derived predominantly from iron monosulfide may not be accurate in terms of predicting the stability of less soluble sulfide complexes of metals of toxicological concern. For example, in a 14-mo field experiment, Liber et al. (1996) found that AVS present in pond sediments as zinc sulfide appeared to be more stable than AVS present as iron sulfide; this was manifested in a concentration-dependent increase in AVS with increasing zinc concentrations, and a relatively smaller variation in temporal changes of AVS in zinc-treated versus control (iron-dominated) samples. This apparent greater stability of zinc sulfide, in comparison to iron sulfide, also has been observed in laboratory toxicity tests with spiked freshwater sediments with exposure durations ranging from 14 to 56 d (Petersen et al., 1996; Sibley et al., 1996). A similar phenomenon also has been noted in experiments with cadmium-spiked marine and freshwater sediments, in which the greater stability of the cadmium sulfide complexes, relative to iron sulfide, was apparently linked to differences in oxidation rates (Di Toro et al., 1996; Hansen et al., 1996b; Peterson et al., 1996). These observations suggest that temporal and spatial variations in AVS likely are dependent upon the dominant metal associated with the sulfides which, at least in the case of zinc and cadmium, might be less variable than suspected based upon studies of iron-dominated systems.

The purpose of the present study was to evaluate this hypothesis in a true field setting where zinc contamination had not been experimentally manipulated. Acid volatile sulfide, SEM and pore water metal concentrations were monitored in zinc-contaminated sediments collected from the same sites at two separate times representing different seasons. We also assessed the toxicity of the sediments in 10-d laboratory toxicity tests with the freshwater amphipod *Hyaella azteca*, in part, to further evaluate the contention that SEM:AVS

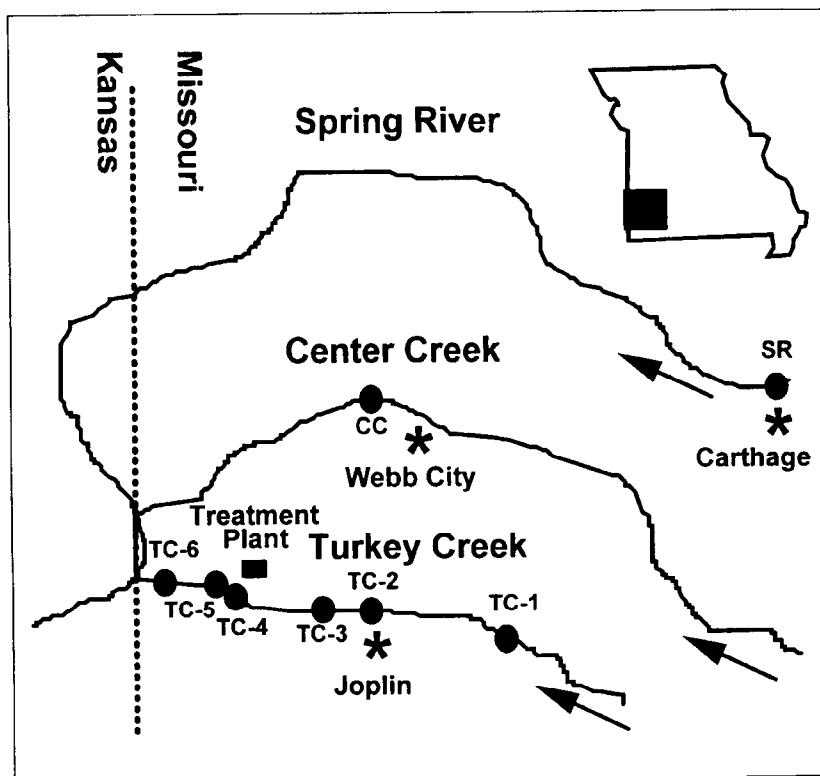


Figure 1. Location of sampling sites within Turkey Creek (TC), Spring River (SR), and Center Creek (CC), Missouri. The arrows indicate direction of water flow.

relationships or pore water metal concentrations are predictive of sediment toxicity.

2. Materials and methods

2.1. Study sites

Six sites within Turkey Creek and one site within each of two neighboring creeks (Center Creek and Spring River) near Joplin, Missouri (Figure 1), with historically different levels of zinc contamination were sampled on two occasions during 1995. The two sampling times (March 8–9 and June 27, 1995) represented distinctly different temperature, and to a lesser extent, dissolved oxygen regimes (Table 1). Sediment characteristics differed among the three creeks. Spring River and Center Creek had soft sediments with a high silt and clay content, and no gravel. Turkey Creek sediments had little silt and clay, and were comprised largely of gravel, pebble, and rock. Some Turkey Creek samples also contained sand and the two furthest downstream

sites (TC-5 and TC-6) had a thin (≤ 1 cm) organic/silt layer on the surface. Analysis of preliminary samples collected during February 1995 had indicated that Spring River sediments had very low SEM (i.e., cadmium, copper, lead, nickel and zinc) levels and thus provided a good negative reference site. Conversely, Center Creek had very high zinc concentrations and low levels of the other four SEM metals, thus providing a positive reference site. Previous analyses in our laboratory had shown that Turkey Creek sediments contained total SEM levels ranging from 37 to 88 $\mu\text{mol/g}$, with zinc comprising 88 to 93% of the total of the five metals (Hansen et al., 1996a).

2.2. Sampling

Sampling locations were chosen to represent possible depositional areas with minimal flow, within 1.5 m of the creek banks. Duplicate or quadruplicate sediment samples for chemical analyses were collected from all eight sites at both sampling times. Sediments were collected in 5 cm diameter acrylic core tubes that were

Table 1. Water quality measurements from sampling sites in Spring River (SR), Turkey Creek (TC), and Center Creek (CC), Missouri at two sampling times

Measurement	March 8–9, 1995			June 27, 1995		
	SR	TC ^a	CC	SR	TC ^a	CC
Depth (cm)	30	15–35	50–60	50–55	25–65	50–60
Temperature (°C)	4.7	2.7–7.4	5.9	18.5	19.0–21.6	18.5
Dissolved oxygen (mg/l)	12.9	10.5–13.0	11.9	8.2	7.2–8.8	8.3
pH	6.9	7.5–8.3	7.0	7.8	6.8–7.8	7.5
Current velocity (m/sec)	0.0	0.0–0.25	0.24	0.0	0.0–0.07	0.18
Clarity	slightly turbid	clear	very turbid	turbid	clear-slightly turbid	very turbid

^a Range over the six sampling sites within Turkey Creek.

12 cm in length. Cores were inserted into the sediments by hand and the top of the tube sealed with a neoprene stopper. The core was carefully lifted out of the sediment and the bottom sealed with a plastic core cap while under water. The neoprene stopper was replaced with another plastic core cap after filling the core with site water. Duplicate cores for the toxicity tests were collected in a similar manner from each site at each sampling time. The sites were generally approached from downstream or perpendicular from shore to prevent disturbance of sampling areas before retrieval of sediment cores. Replicate core samples from each site were collected from within a 1 to 2 m² sampling area. Cores were placed in coolers containing dry ice for transport to the laboratory. Cores for chemistry were stored frozen, and the toxicity test samples were held at 4°C until analysis.

2.3. Chemical analyses

In the laboratory, sediment cores for chemical analysis were partially thawed, extruded from the tubes with a plunger, and cut into two sections (0–3 and 3–6 cm) in a glove box containing a nitrogen atmosphere. Each sediment section was homogenized and subsamples collected for AVS and SEM analyses. Other homogenized subsamples were centrifuged for 30 min at 10,000 × g to isolate pore water (Ankley & Schubauer-Berigan, 1994). The pore water was filtered through an acid washed 0.45 µm membrane filter and acidified to 1% (v/v) with nitric acid prior to instrumental analysis. Due to the sandy nature of several of the sediments, it was not always possible to isolate adequate volumes of pore water for metal determinations.

Methods of AVS extraction and analysis were similar to those described by Allen et al. (1993).

Briefly, 15 to 20 g of homogenized sediment from individual core sections was placed in a reaction flask containing 200 ml of deoxygenated, deionized water. After purging the apparatus with nitrogen for 15 min, 20 ml of deoxygenated 6 M hydrochloric acid was added to the reaction flask and nitrogen bubbled through the system for 1 h. Sulfide (as hydrogen sulfide) freed from the sediment passed through a buffer solution and was trapped in a silver nitrate solution, and the resultant silver sulfide precipitate was quantified gravimetrically. The mean recovery of AVS was 83% from sulfide-spiked water samples, and the mean percent agreement between duplicate (split sample) analyses was 72%.

The acidified sediment-water mixture remaining in the AVS reaction flask was used for SEM analysis. After allowing sediment particles to settle, the supernatant was decanted, vacuum filtered through a 0.45 µm mixed cellulose ester membrane filter, and diluted to 250 ml. The recovered solution was analyzed for zinc with an Instrumentation Laboratories Video 12 Atomic Absorption Spectrophotometer (AAS) with an air-acetylene flame. The mean agreement for analysis of simultaneously-extracted zinc for duplicate (split) samples was 79%. Pore water zinc and other potentially toxic SEM (cadmium, copper, lead, nickel) also were analyzed using flame AAS.

2.4. Toxicity tests

Ten-d sediment bioassays were performed with *H. azteca* using the duplicate sediment cores collected from the different creek sites on the two sampling dates. Tests were run after sediments had been transferred to 300 ml-high form beakers, taking care to maintain sediment profiles as intact as possible. Bioassays were

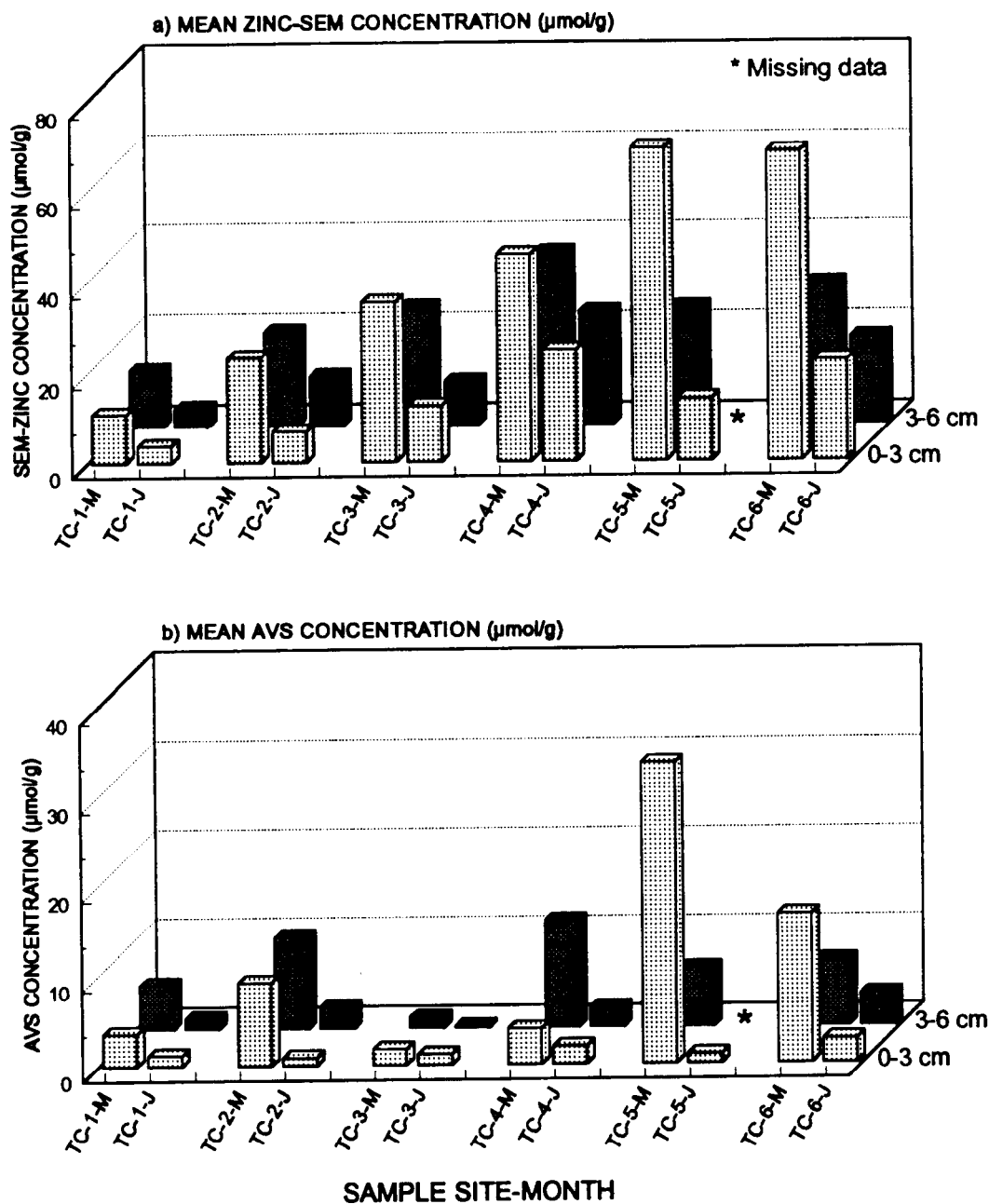


Figure 2. (a) Mean zinc-SEM concentrations and (b) mean AVS concentrations in 0–3 and 3–6 cm horizons of sediment cores collected from six sites within Turkey Creek, Missouri on March 8–9 (M) and June 27 (J), 1995.

performed at $23 \pm 1^\circ\text{C}$ in a test system (Benoit et al., 1993) that provided from 2.3 to 4.6 volume renewals of clean overlying water daily. The water source for the tests was dechlorinated municipal water from the city of Superior, Wisconsin. Ranges of general water quality characteristics during the tests were: pH, 7.2 to 8.1;

alkalinity, 42.4 to 69.4 mg/L as CaCO_3 ; hardness, 50.0 to 62.2 mg/L as CaCO_3 ; and dissolved oxygen, 3.2 to 7.6 mg/L. There were 10 *H. azteca* per beaker and the test endpoints was survival. Each beaker received 1.0 mg of a yeast-Cerophyll-trout chow food mixture daily (Ankley et al., 1993).

Table 2. Differences between zinc-SEM and AVS concentrations ($\mu\text{mol/g}$), corresponding pore water zinc concentrations ($\mu\text{mol/l}$), and mean survival of *Hyaella azteca* in 10-d sediment toxicity tests with sediment cores collected from the various sampling sites during March and June, 1995. Analytical data are indicated as \bar{x} (SD) for duplicate or quadruplicate samples/site

Site	March 8–9, 1995					June 27, 1995				
	[Zn-SEM]-[AVS]		Pore water [Zn]		Mean <i>H. azteca</i> survival (%)	[Zn-SEM]-[AVS]		Pore water [Zn]		Mean <i>H. azteca</i> survival (%)
	0–3 cm	3–6 cm	0–3 cm	3–6 cm		0–3 cm	3–6 cm	0–3 cm	3–6 cm	
SR	1.2 (0.0)	1.2 (0.4)	0.1	0.2	90	0.0	–1.2 (1.0)	1.0	1.4	100
TC-1	7.3 (1.4)	7.5 (1.5)	1.9 (1.8)	1.0 (0.8)	95	2.7 (0.2)	3.0 (0.2)	–	–	80
TC-2	14.1 (3.3)	10.7 (1.2)	0.6 (0.2)	0.9 (0.6)	70	6.0 (1.9)	8.6 (0.9)	–	–	85
TC-3	33.8 (4.3)	25.0 (3.3)	3.6 (0.8)	8.6 ^b	60	11.3 (6.9)	9.6 ^b	–	–	50
TC-4	42.0 (11.5)	26.1 (0.9)	– ^a	–	80	22.8 (9.8)	22.8 (5.9)	–	–	5
TC-5	35.8 (0.8)	19.3 (6.5)	0.7 (0.0)	–	35	12.9 (2.7)	† ^c	–	–	30
TC-6	52.1 (12.4)	23.7 (4.2)	7.5 (3.5)	–	15	19.6 (3.6)	15.6 (7.2)	–	–	60
CC	114.3 (29.8)	127.5 (22.2)	24.5 (11.9)	44.2 (34.2)	0	92.4 (5.7)	103.3 (20.3)	9.9	–	0

^a Unable to isolate enough pore water for analysis.

^b Single measurement.

^c Unable to collect 3–6 cm deep sediments.

2.5. Statistics

Relationships between simultaneously-extracted zinc versus AVS concentrations were evaluated using linear regression. Due to the small sample size for the toxicity assays ($n = 2$), survival data were not evaluated statistically. Mortality in the test samples was considered elevated when it exceeded 20% (Ankley et al., 1993). The pore water zinc concentration associated with 50% mortality of *H. azteca* (LC50) was calculated using the trimmed Spearman-Kärber technique (Hamilton et al., 1977).

3. Results

Zinc concentrations in Spring River sediments were always low and concentrations in Center Creek were always very high (data not shown). Simultaneously-extracted zinc concentrations in Turkey Creek sediments generally increased with increasing downstream distance (Figure 2a). There was a pronounced decrease in zinc concentrations in solid-phase sediment in June

as compared to March at all sampling sites within Turkey Creek and, in March, zinc concentrations were generally higher in the 0–3 cm horizon as compared to the 3–6 cm horizon (Figure 2a).

Similar to previous studies (Hansen et al., 1996a), zinc comprised $91 \pm 4.1\%$ of the total SEM in the Turkey Creek sediment samples over the course of the study. Lead accounted for $7.2 \pm 2.8\%$ and cadmium, copper, and nickel together for $< 2\%$ of the SEM. Since zinc accounted for the vast majority of SEM in all sediment samples, comparisons with AVS concentrations and toxicity were made for zinc, rather than total SEM.

Acid volatile sulfide concentrations in Turkey Creek were also lower in June than in March. On both occasions the highest concentrations were measured downstream from the sewage treatment plant (Figure 2b). In general, AVS concentrations in the 0–3 cm horizon upstream from the sewage treatment plant were lower than in the 3–6 cm horizon, whereas the opposite was generally true downstream from the plant. The AVS concentrations in both Spring River and Center

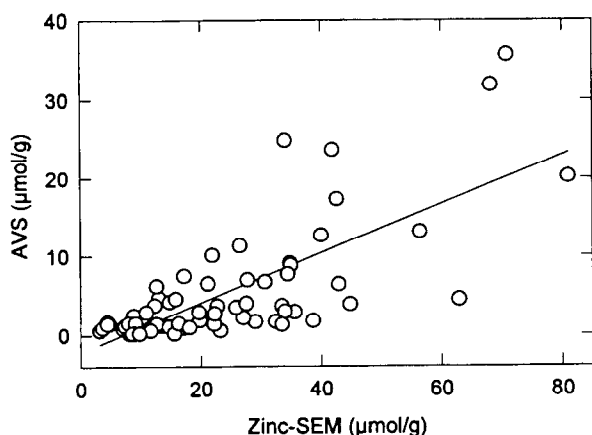


Figure 3. Relationships between zinc-SEM and AVS concentrations in sediment cores collected from six sites within Turkey Creek.

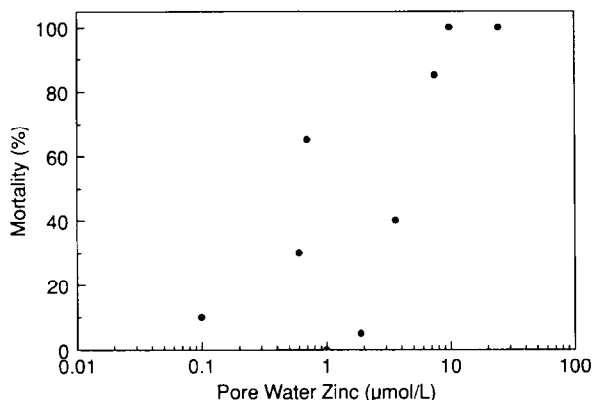


Figure 4. Sediment toxicity to *Hyaella azteca* versus pore water zinc concentrations.

Creek were generally much lower than those in Turkey Creek (data not shown).

Although the data were variable, a significant positive relationship existed between simultaneously-extracted zinc and AVS concentrations in the Turkey Creek sediment samples (Figure 3). The least square linear regression for the combined March and June data from all horizons was highly significant ($p < 0.0002$) and yielded an $r^2 = 0.53$.

Virtually all the sediment samples had a molar difference in simultaneously extracted zinc minus AVS that was greater than 0 (Table 2). In March, but not June these differences were usually greater in the 0–3 cm horizon than in the 3–6 cm segment. Zinc was always detected in the pore water, when it could be isolated (Table 2).

Results from the *H. azteca* toxicity tests indicated that samples from Center Creek and Turkey Creek downstream from the treatment plant caused elevated ($> 20\%$) mortality at both sampling times (Table 2). Samples from Turkey Creek stations TC-3 and TC-4 also were toxic in June. Toxicity for each sampling period generally was observed at the largest surficial (0–3 cm) molar zinc-SEM:AVS differences. Also, there was a positive relationship between pore water zinc concentrations in the surficial sediments and mortality of *H. azteca* (Figure 4). Based on these data, the pore water zinc LC50 (95% CI) was 2.64 (1.76 to 3.96) $\mu\text{mol/L}$.

4. Discussion

The objective of this study was to evaluate, in a field setting, the stability of AVS present as zinc versus iron sulfides from the standpoint of oxidative processes related to temporal (seasonal) and/or spatial (depth) variations. Our approach was to sample a range of sites, varying in zinc contamination, during late winter and early summer. For this particular design to have optimal sensitivity, the sites should have varying zinc concentrations, and a relatively constant amount of AVS, some of which would be present as zinc sulfide and some of which would be present as iron sulfide. Unfortunately this was not the case in our study because, even though zinc varied by approximately a factor of five across the Turkey Creek sites, virtually all the samples had more simultaneously extracted zinc than AVS. Thus, based upon solubility products of the two metal-sulfides, very little if any of the AVS likely was comprised of iron sulfide complexes (Di Toro et al. 1992). In fact, there was a significant positive correlation ($r^2 = 0.53$) between the amount of zinc in the sediments and the amount of AVS, suggesting that the system was dominated by zinc sulfide as opposed to other metal sulfides. In any case, the lack of samples containing appreciable AVS as iron sulfide precludes direct comparison of relative metal-sulfide stability.

An alternative approach to assessing the zinc:AVS relationships would be to compare samples across seasons with the hypothesis that, if the zinc sulfides were relatively stable, less seasonal variability in AVS would occur than that noted in iron-dominated (uncontaminated) sediments (e.g., Leonard et al., 1993; Howard & Evans, 1993). However, this analysis also was not feasible in the present study because zinc concentrations, which were highly correlated with those of AVS,

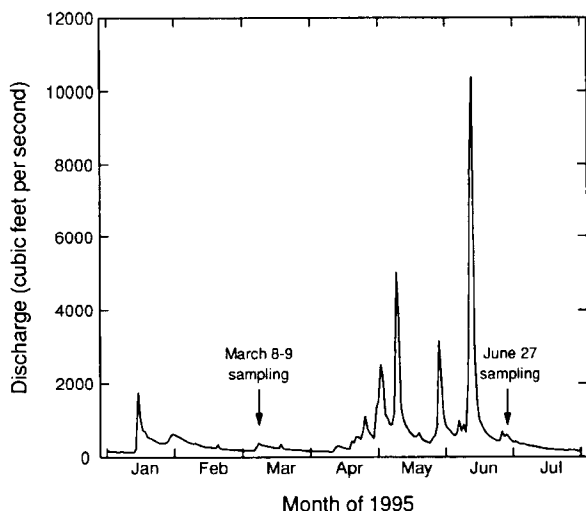


Figure 5. Daily water discharge for Center Creek below Carl Junction, Missouri. Data were collected by the U.S. Geological Survey.

changed markedly between the two sampling times, with concentrations in June lower than those in March. This suggests that there were distinct changes in surficial sediments between the two sampling periods. A U.S. Geological Survey gauging station on Center Creek indicated a major storm event in the area about 2 wk before the June 27 sampling period, which may have flushed surficial sediments from the Turkey Creek system (Figure 5).

A final possibility for examining the stability of zinc sulfides in the Turkey Creek sediments would be to consider zinc:AVS relationships in surficial (0–3 cm) versus deeper (3–6 cm) sediments, within each of the two different sampling periods. Surficial concentrations of AVS comprised of iron sulfides typically are smaller than in deeper sediments (e.g., Howard & Evans 1993; Hare et al., 1994; Hansen et al., 1996b; Leonard et al., 1996). In the present study it is difficult to directly compare depth-dependent differences in AVS because the zinc and AVS concentrations were positively correlated, and zinc also varied with depth. However, to “normalize” for this effect, we developed a relative stability index (RSI) using horizon-specific zinc:AVS ratios. To do this we calculated, for each sample, the ratio of the zinc:AVS ratio in the 0–3 cm horizon to the corresponding value in the 3–6 cm horizon. Specifically:

$$\text{RSI} = (\text{Zn-SEM/AVS})_{0-3} / (\text{Zn-SEM/AVS})_{3-6}$$

Theoretically, if there were minimal surficial oxidation of AVS, relative to the deeper sediments, the RSI should be close to one. The mean RSI (\pm standard error of the mean) obtained for the March sampling period was $1.4 (\pm 0.41, n = 5)$ while the mean value for June was $1.0 (\pm 0.18, n = 5)$. These data suggest that, upon accounting for horizon-specific variations in simultaneously-extracted zinc, there was little difference in AVS concentrations between surficial versus deeper sediments.

Because virtually all the test samples had more simultaneously-extracted zinc than AVS, it was impossible to use the present data set to evaluate the contention that no toxicity occurs when there is more AVS than SEM (Ankley et al., 1994; 1996). We did observe, however, that significant toxicity to *H. azteca* usually was seen in samples with the largest zinc:AVS differences. We also observed that toxicity was correlated with pore water zinc concentrations, which is consistent with previous studies concerning metal bioavailability in sediments (see Ankley et al. 1996, and references therein). The LC50 for *H. azteca*, based upon pore water zinc concentrations, was $2.64 \mu\text{mol/L}$. The LC50 for *H. azteca* in 10-d water-only tests conducted in Lake Superior water, under conditions otherwise similar to those used in the sediment tests, is approximately 2.5-fold lower at $1.12 \mu\text{mol/L}$ (Phipps et al., 1995). This difference in LC50 values could be due to variations in hardness and/or concentrations of dissolved (metal-complexing) ligands between Turkey Creek sediment pore water and Lake Superior water. It should be noted that the correlation between toxicity and pore water zinc concentrations does not necessarily indicate that zinc was the only factor contributing to toxicity; for example, concentrations of PAHs and organochlorine pesticides were elevated in certain of the sediments, particularly those downstream of the treatment plant (CGI, unpublished data).

5. Summary and conclusions

In summary, this study reinforces the necessity of considering metal-specific sulfide interactions when attempting to predict the bioavailability and toxicity of metals in aquatic sediments. Sediments in the Turkey Creek system clearly are dominated by zinc, as opposed to iron sulfides, the former of which might be less susceptible to oxidation than the latter. This differential stability is important in considering the potential for release of sulfide-bound metals associated with sea-

sonal or spatial variations in sulfide oxidation/sulfate reduction. Data from the present study also confirm the observation that toxicity of metal-contaminated sediments can be correlated with interstitial water metal concentrations.

This study also demonstrates the complexity that can occur in the field, particularly from the standpoint of assessing seasonal variations in sediment quality. For example, previous studies, primarily in lake systems, had suggested that minimal AVS concentrations might be expected in cold-, as opposed to warm-weather periods; however, the opposite trend was seen in this study, i.e., in the stream under consideration, AVS concentrations were higher in March than in June. But this may well have resulted from alterations in the character of the sediments (as evidenced by the concurrent decrease in zinc concentrations), related to scouring of surficial layers by storm event(s), rather than to more subtle seasonal variations in temperature or redox conditions.

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References

- Adams, W.J., R.A. Kimerle & R. G. Mosher, 1985. Aquatic safety assessment of chemicals sorbed to sediments. In: R.D. Cardwell, R. Purdy & R. G. Bahner (eds), *Aquatic toxicology and hazard assessment: Seventh symposium*. STP 854. American Society for Testing and Materials, Philadelphia, PA, pp. 429–453.
- Allen, H.S., G. Fu & B. Deng, 1993. Analysis of acid-volatile sulfide (AVS) and simultaneously extracted metal (SEM) for the estimation of potential toxicity in aquatic sediments. *Environ. Toxicol. Chem.* 12: 1441–1453.
- Ankley, G.T. & M.K. Schubauer-Berigan, 1994. Comparison of techniques for the isolation of pore water for sediment toxicity testing. *Arch. Environ. Contam. Toxicol.* 27: 507–512.
- Ankley, G.T., G.L. Phipps, E.N. Leonard, D.A. Benoit, V.R. Mattson, P.A. Kosian, A.M. Cotter, J.R. Dierkes, D.J. Hansen & J.D. Mahony, 1991. Acid-volatile sulfide as a factor mediating cadmium and nickel bioavailability in contaminated sediments. *Environ. Toxicol. Chem.* 10: 1299–1307.
- Ankley, G.T., R.A. Hoke, D.A. Benoit, E.M. Leonard, C.W. West, G.L. Phipps, V.R. Mattson & L.A. Anderson, 1993. Development and evaluation of test methods for benthic invertebrates and sediments: Effects of flow rate and feeding on water quality and exposure conditions. *Arch. Environ. Contam. Toxicol.* 25: 12–19.
- Ankley, G.T., N.A. Thomas, D.M. Di Toro, D.J. Hansen, J.D. Mahony, W.J. Berry, R.C. Swartz & R.A. Hoke, 1994. Assessing potential bioavailability of metal in sediments: A proposed approach. *Environ. Manage.* 18: 331–337.
- Ankley, G.T., D.M. Di Toro, D.J. Hansen & W. J. Berry, 1996. Technical basis and proposal for deriving sediment quality criteria for metals. *Environ. Toxicol. Chem.* In Press.
- Benoit, D.A., G.L. Phipps & G.T. Ankley, 1993. A sediment testing intermittent renewal system for the automated renewal of overlying water in toxicity tests with contaminated sediments. *Water Res.* 27: 403–412.
- Berry, W.J., D.J. Hansen, J.D. Mahony, D.L. Robson, D.M. Di Toro, B.J. Shipley, B. Rogers & J.M. Corbin, 1996. Predicting the toxicity of metals-spiked laboratory sediments using acid volatile sulfide and interstitial water normalizations. *Environ. Toxicol. Chem.* In Press.
- Besser, J.M., C.G. Ingersoll & J.P. Giesy, 1996. Effects of spatial and temporal variability of acid volatile sulfide on the bioavailability of copper and zinc in freshwater sediments. *Environ. Toxicol. Chem.* 15: 286–293.
- Brumbaugh, W.G., C.G. Ingersoll, N.E. Kemble, T.W. May & J.L. Zajicek, 1994. Chemical characterization of sediments and pore water from the upper Clark Fork River and Milltown Reservoir, Montana. *Environ. Toxicol. Chem.* 13: 1971–1983.
- Carlson, A.R., G.L. Phipps, V.R. Mattson, P.A. Kosian & A.M. Cotter, 1991. The role of acid-volatile sulfide in determining cadmium bioavailability and toxicity in freshwater sediments. *Environ. Toxicol. Chem.* 10: 1309–1319.
- Casas, A.M. & E.A. Crecelius, 1994. Relationship between acid volatile sulfide and the toxicity of zinc, lead and copper in marine sediments. *Environ. Toxicol. Chem.* 13: 529–536.
- Cornwell, J.C. & J.W. Morse, 1987. The characterization of iron sulfide minerals in anoxic marine sediments. *Mar. Chem.* 22: 193–206.
- De Witt, T.H., R.C. Swartz, D.J. Hansen, W.J. Berry & D. McGovern, 1996. Interstitial metal and acid volatile sulfide predict the bioavailability of cadmium during a full life cycle sediment toxicity test using the estuarine amphipod, *Leptocheirus plumulosus*. *Environ. Toxicol. Chem.* In Press.
- Di Toro, D.M., J.D. Mahony, D.J. Hansen, K.J. Scott, M.B. Hicks, S.M. Mayr & M.S. Redmond, 1990. Toxicity of cadmium in sediments: The role of acid volatile sulfide. *Environ. Toxicol. Chem.* 9: 1487–1502.
- Di Toro, D.M., C.S. Zarba, D.J. Hansen, W.J. Berry, R.C. Swartz, C.E. Cowan, S.P. Pavlou, H.E. Allen, N.A. Thomas & P.R. Paquin, 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ. Toxicol. Chem.* 10: 1541–1583.
- Di Toro, D.M., J.D. Mahony, D.J. Hansen, K.J. Scott, A.R. Carlson & G.T. Ankley, 1992. Acid volatile sulfide predicts the

- acute toxicity of cadmium and nickel in sediments. *Environ. Sci. Technol.* 26: 96–101.
- Di Toro, D.M., J.D. Mahony, D.J. Hansen & W.J. Berry, 1996. A model of the oxidation of iron and other metal sulfides in sediments. *Environ. Toxicol. Chem.* In Press.
- Hamilton, M.A., R. C. Russo & R. V. Thurston, 1977. Trimmed Spearman-Kärber technique for estimating median lethal concentrations in toxicity bioassays. *Environ. Sci. Technol.* 7: 714–719. Correction 12: 417 (1978).
- Hansen, D.J., W.J. Berry, J. D. Mahony, W. S. Boothman, D. L. Robson, G.T. Ankley, D. Ma, Q. Yan & C.E. Pesch, 1996a. Predicting toxicity of metal-contaminated field sediments using interstitial water concentrations of metals and acid-volatile sulfide normalization. *Environ. Toxicol. Chem.* In Press.
- Hansen, D.J., J.D. Mahony, W.J. Berry, S.J. Benyi, J.M. Corbin, S.D. Pratt & M.B. Able, 1996b. Chronic effect of cadmium in sediments on colonization by benthic marine organisms: An evaluation of the role of interstitial cadmium and acid volatile sulfide on biological availability. *Environ. Toxicol. Chem.* In Press.
- Hare, L., R. Carignan & M.A. Huerta-Diaz, 1994. A field study of metal toxicity and accumulation by benthic invertebrates: Implications for the acid-volatile sulfide (AVS) model. *Limnol. Oceanogr.* 39: 1653–1668.
- Herlihy, A.T. & A.L. Mills, 1985. Sulfate reduction in freshwater sediments receiving acid mine drainage. *Appl. Environ. Microbiol.* 49: 179–186.
- Howard, D.E. & R.D. Evans, 1993. Acid-volatile sulfide (AVS) in a seasonally anoxic mesotrophic lake: Seasonal and spatial changes in sediment AVS. *Environ. Toxicol. Chem.* 12: 1051–1057.
- Leonard, E.N., V.R. Mattson, D.A. Benoit, R.A. Hoke & G.T. Ankley, 1993. Seasonal variation of acid volatile sulfide in sediment cores from three northeastern Minnesota lakes. *Hydrobiologia* 271: 87–95.
- Leonard, E.N., G. T. Ankley & R.A. Hoke, 1996. Evaluation of metal concentrations in marine and freshwater surficial sediments from the Environmental Monitoring and Assessment Program relative to proposed sediment quality criteria for metals. *Environ. Toxicol. Chem.* In Press.
- Liber, K., D. Call, T. Markee, K. Schmude, M. Balcer, F. Whiteman & G. T. Ankley, 1996. Effects of acid volatile sulfide on zinc bioavailability and toxicity to benthic macroinvertebrates in spiked-sediment field experiments. *Environ. Toxicol. Chem.* In Press.
- Luoma, S.N. & J.L. Carter, 1993. Understanding the toxicity of contaminants in sediments: Beyond the bioassay-based paradigm. *Environ. Toxicol. Chem.* 12: 793–796.
- Meyer, J. S., W. Davison, B. Sundby, J.T. Oris, D.J. Lauren, U. Förstner, J. Hong & D.G. Crosby, 1994. The effects of variable redox potentials, pH and light on bioavailability in dynamic water-sediment environments. In: J.L. Hamelink, P.F. Landrum, H.L. Bergman & W.H. Benson (eds), *Bioavailability: Physical, Chemical and Biological Interactions*. CRC Press, Boca Raton, FL, pp. 155–170.
- Pesch, C.E., D.J. Hansen, W.S. Boothman, W.J. Berry & J.D. Mahony, 1995. The role of acid-volatile sulfide and interstitial water metal concentrations in determining bioavailability of cadmium and nickel from contaminated sediments to the marine polychaete *Neanthes arenaceodentata*. *Environ. Toxicol. Chem.* 14: 129–141.
- Peterson, G.S., G.T. Ankley & E.N. Leonard, 1995. Effect of bioturbation on metal-sulfide oxidation in surficial freshwater sediments. *Environ. Toxicol. Chem.* In Press.
- Phipps, G.L., V.R. Mattson & G.T. Ankley, 1995. Relative sensitivity of three freshwater benthic invertebrates to ten contaminants. *Arch. Environ. Contam. Toxicol.* 28: 281–286.
- Sibley, P.K., G.T. Ankley, A.M. Cotter & E.N. Leonard, 1996. Predicting chronic toxicity of sediments spiked with zinc: An evaluation of the acid volatile sulfide (AVS) model using a life cycle test with the midge *Chironomus tentans*. *Environ. Toxicol. Chem.* In Press.
- Slotton, D.G. & J.E. Reuter, 1995. Heavy metals in intact and resuspended sediments of a California reservoir, with emphasis on potential bioavailability of copper and zinc. *Mar. Freshwater Res.* 46: 257–265.
- Swartz, R.C., G.R. Ditsworth, D.W. Schults & J.O. Lamberson, 1985. Sediment toxicity to a marine infaunal amphipod: Cadmium and its interaction with sewage sludge. *Mar. Environ. Res.* 18: 133–153.